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THERMODYNAMICS OF MOLYBDENUM ADSORPTION ONTO POROUS COPOLYMER

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Abstract

Macroporous glycidyl methacrylate and ethylene glycol dimethacrylate copolymer functionalized with diethylene triamine, PGME-deta, was tested as molybdate ion adsorbent from aqueous solutions. Kinetics of Mo(VI) sorption was investigated in batch static experiments, in the temperature range 298-343 K. The temperature rise promotes Mo(VI) removal, with the maximum experimental adsorption capacity of 585 mg g^{-1} at 343 K. Thermodynamic parameters revealed spontaneous and endothermic nature of Mo(VI) adsorption onto PGME-deta.

Introduction

Molybdenum is the most concentrated trace element in the seawater due to its stability and weak adsorption behavior [1]. It is essential for some biological functions in plants and animals. Its compounds exhibit all oxidation states from +2 to +6 with the predominant Mo(IV) and Mo(VI) [2]. Since high concentrations of molybdate (>5 ppm) cause an environmental problem, the removal of mainly anionic molybdenum species from wastewater and groundwater becomes greatly significant. Macroporous PGME-deta seems to be a very promising adsorbent for the removal of toxic pollutants which, depending on pH, proved to be adaptable for adsorption of cations, like Cu(II) and Co(II) at pH 5.5 [3] and anions of Pt(IV), Au(III) and Rh(III) [4], Cr(VI) [5]. In this paper, macroporous PGME-deta was used as adsorbent for molybdenum anion species. Kinetic data for Mo(VI) removal on PGME-deta was collected at different temperatures and the thermodynamic parameters were evaluated.

Experimental

PGME-deta (surface area 29 m^2g^{-1}, specific pore volume 0.89 cm^3g^{-1}, pore diameter 212 nm, particle size 150-300 μm, amino groups concentration 6.51 $mmolg^{-1}$), obtained as described elsewhere [5] was used in molybdenum adsorption experiments. The sorption kinetics of Mo anions from acidic aqueous solutions (C_i= 0.1M; pH=2) was investigated in batch experiments at different temperatures. Copolymer (0.50 g) was contacted with 50 mL of Mo salt solution. Aliquots (0.5 mL) were removed at appropriate times, diluted and analyzed by ICP-AES (Perkin Elmer, Model ICP 400).

Results And Discussion

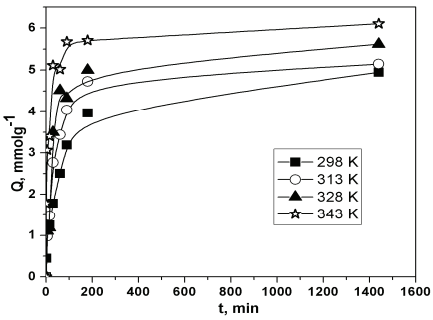

Fig. 1. Effect of temperature on Mo(VI) adsorption rate on PGME-deta.

The adsorption of Mo anion can be interpreted based on PGME-deta surface charge and the nature of the molybdenum anionic species. At pH<6, the heptamolybdate $Mo_7O_{24}^{6-}$ polyanion exists [1]. Since the amino groups ($–NH_2$) of PGME-deta are in protonated cationic form ($–NH_3^+$) to a high extent in acidic solution, the copolymer surface is positively charged and electrostatic interaction (the initial step in the binding mechanism) occurs between the sorbent and molybdenum anions resulting in superior Mo(VI) uptake. The temperature rise promotes Mo(VI) sorption by PGME-deta (Fig. 1), with the maximum experimental sorption capacity of 585 mg g^{-1} at 343 K. Thermodynamic considerations of an adsorption process are necessary to establish whether the process is spontaneous or not. The used equations are listed in Table 1.

Table 1. Thermodynamics equations.

Apparent equilibrium constant equation	$\log K_c = \frac{F_e}{1 - F_e}$	[6]
Van't Hoff equation	$\log Kc = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT}$	[6]
Arrhenius equation (linearized)	$\ln k_2 = \ln A - \frac{E_a}{RT}$	[7]

Where: K_c - equilibrium constant, F_e -fraction adsorbed at equilibrium, ΔS-entropy change (kJ mol^{-1} K^{-1}), R-universal gas constant (8.314 J mol^{-1} K^{-1}), ΔH-enthalpy change (kJ mol^{-1}), T- temperature (K), k_2 -pseudo-second order rate constant ($g^{-1}mmol^{-1}min^{-1}$), A-Arrhenius factor and E_a-activation energy (kJ mol^{-1}). The data obtained for Mo(VI) adsorption at various temperatures were used for calculating the thermodynamic parameters (Table 2). Results show positive ΔH value and increase of Mo(VI) adsorption with temperature, both characteristics of chemical adsorption (endothermic process). Mo(VI) anion is likely at first adsorbed by electrostatic (physisorption) interactions. Thus, both processes occur with chemisorption being predominant, possibly due to the transition metal nature of Mo; during adsorption process *d* orbitals become filled with electrons from nitrogen or oxygen from PGME-deta. The negative Gibbs free energy change (ΔG) indicates spontaneous Mo(VI) adsorption onto PGME-deta. Value of ΔG is negative only because of ΔS positive contribution again indicative of chemisorption ($\Delta G=\Delta H-T\Delta S$). This contribution increases with temperature elevation, suggesting improved adsorption at higher temperatures.

Table 2. Thermodynamic parameters for Mo(VI) sorption onto PGME-deta.

T, K	ΔG, kJ mol^{-1}	E_a, kJ mol^{-1}	$T\Delta S$, kJ mol^{-1}	ΔH, kJ mol^{-1}
298	-3.78	22.3	25.7	19.6
313	-5.08		27.0	
328	-6.37		28.3	
343	-7.67		29.6	

The positive ΔS value reflects an increase in randomness at the solid/solution interface expected to occur during chemsorption of Mo(VI) onto PGME-deta [1].

When sorption rate is governed by intraparticle diffusion mechanism, activation energy is low and within the range of values of 8–22 kJ mol^{-1} [8]. In this case, calculated E_a value is only marginally higher than 22 kJ mol^{-1}. Considering that the sorption capacity increased with temperature, this may indicate that chemisorption process is rate-controlling as well as pore diffusion.

Conclusion

Kinetics of Mo(VI) adsorption onto macroporous PGME-deta was investigated in the temperature range 298-343 K. Thermodynamic parameters revealed spontaneous and endothermic nature of Mo(VI) adsorption, with increased randomness in the system. The temperature rise promotes Mo(VI) removal.

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